Reconsideration of the excited-state double proton transfer (ESDPT) in 2-aminopyridine/acid systems: role of the intermolecular hydrogen bonding in excited states

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In the present work, the excited-state double proton transfer (ESDPT) in 2-aminopyridine (2AP)/acid systems has been reconsidered using the combined experimental and theoretical methods. The steady-state absorption and fluorescence spectra of 2AP in different acids, such as formic acid, acetic acid, propionic acid, *etc.* have been measured. We demonstrated for the first time that the ESDPT reaction can take place between 2AP and all of these acids due to the formation of the intermolecular double hydrogen bonds. Furthermore, the vitally important role of the intermolecular double hydrogen bonds between 2AP and acids for ESDPT reaction has also been confirmed by the disappearance of ESDPT when we add the polar acetonitrile to the 2AP/acids systems. This may be due to that the respective polar solvation of 2AP and acids by the acetonitrile solvent disrupts the formation of intermolecular double hydrogen bonds between 2AP and acids. Moreover, the intermolecular double hydrogen bonds are demonstrated to be significantly strengthened in the electronic excited state of 2AP/acid systems using the time-dependent density functional theory (TDDFT) method. The ESDPT reaction is facilitated by the electronic excited-state hydrogen bond strengthening. In addition, potential energy curves of the electronic excited state along the proton transfer coordinate are also calculated by the TDDFT method. The stepwise mechanism of the ESDPT reaction in the 2AP/acid systems is theoretically reconfirmed, and the concerted mechanism is theoretically excluded. At the same time, the sequence of the double proton transfers is theoretically clarified for the first time using the potential energy curves calculated by TDDFT method.

I. Introduction

The photoinduced tautomerism reaction is one of the most elementary processes in photochemistry. It has been widely investigated by various theoretical and experimental methods during past several decades.[1–7] Two kinds of tautomerism are possible and common in biochemistry systems, one is the transformation between enol and keto forms, the other is the transition from the amino compounds to the imino ones.

The excited-state hydrogen bonding and the role of hydrogen bonding in the electronic excited state on the photophysics and photochemistry have been paid more and more attention in recent years.[8–21] In our recent works, we have demonstrated for the first time that the intermolecular hydrogen bonding in electronic excited states can dynamically tune the photophysics and photochemistry of chromophores in hydrogen bonding surroundings.[8–15] For example, the internal conversion (IC) and the solute–solvent intermolecular photoinduced electron transfer (PET) are significantly facilitated by intermolecular hydrogen bonding due to the strengthening or weakening of hydrogen bonding in electronic excited states. The intermolecular hydrogen bonding between hydrogen donor and acceptor molecules may be strong enough to induce the intermolecular proton transfer reaction, which could directly influence the molecular structures and reactivity.

Proton transfer reactions have received a great deal of attention recently because of the ubiquity in molecular science, it is conducive to hydrogen atom exchange in acid/base complex and solute/solvent systems.[22–45] Among the many known proton-transfer reactions, excited-state double proton transfer (ESDPT) reaction in the double hydrogen-bonded complex has been of considerable interest.[21–34] In protic solvents, proton-transfer reactions induced by photoexcitation are facilitated by strong intermolecular interaction between the solute and solvent. Proton transfer reactions in nitrogen-containing heterocyclic molecules are particularly relevant to biochemical system. The spectroscopy and dynamics information could be significant to investigate the reaction mechanism.[35–45]

As a typical amino–imino tautomerism example, 2-amino-pyridine (2AP) has drawn much attention of several groups.[34,46–52] It has been reported that ESDPT can take place in the 2AP/acetic acid system due to the formation of the intermolecular double hydrogen bonds. In this

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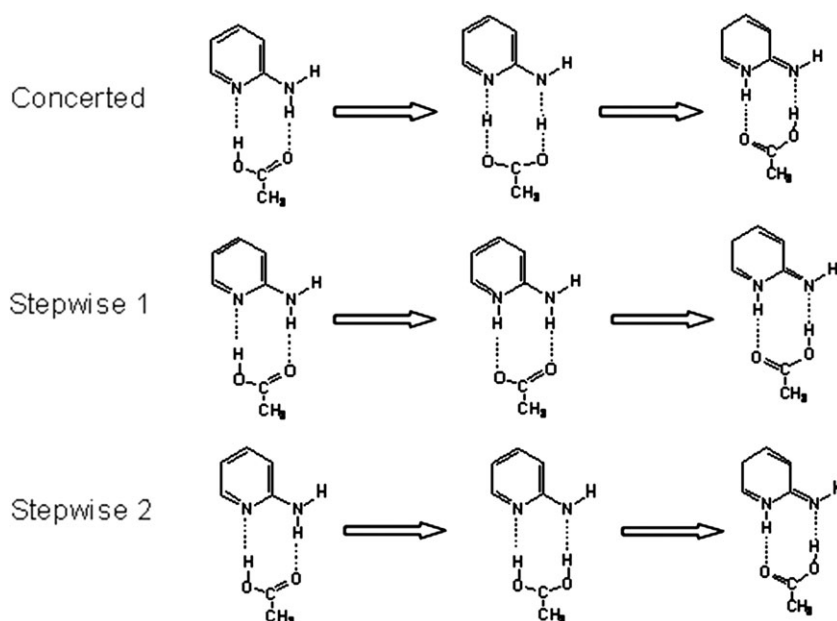
Scheme 1 Three types of the excited-state double proton transfer (ESDPT) reaction mechanism.

phototautomerism, acetic acid acts as a catalyst. Ishikawa *et al.* have investigated this host–guest system, providing experimental results of picosecond dynamics.[34] The ion-pair intermediate has been unambiguously identified by its fluorescence spectrum. They found that the first proton transfer is too fast to detect and the second proton is transferred with a rise time of 5 ps.[34] Hung *et al.* have performed theoretical calculations on the ground and exited states double proton transfer of this 2AP/acetic acid system.[52] These works are lean to the stepwise ESDPT mechanism for the 2AP/ACID system in both experiments and computations. Although the two-step reaction mechanism has been authentic due to the existence of an identifiable zwitterionic, the sequence of the asynchronous double proton transfer is still worth to be confirmed further.

Three types of possible ESDPT processes are shown in Scheme 1. In the concerted mechanism, one proton transfers along O–H···N, and the other moves along N–H···O. The two protons transfer concertedly. Namely, when one proton is moving, the other is also transfers along the intermolecular hydrogen bond correspondingly. The stepwise mechanism is distinctly divided into two types. The stepwise 1 refers that one proton transfers from the O–H group of acid to the ring nitrogen of 2AP along the hydrogen bond O–H···N to form an ion-pair of the protonated 2AP cation and the acid anion. After the arrival of the first proton to the ring nitrogen, the other proton starts to move from the amino part to the acetic acid, and then the imino tautomer is formed. The stepwise 2 refers the opposite sequence of proton transfers.

In the present work, we have measured the steady-state absorption and fluorescence spectra of the 2AP/acid systems and carried out the theoretical calculations to study the photoinduced proton transfer process and then discussed the mechanism in details. We focused our attention on the role of intermolecular hydrogen bonding in electronic excited states on the ESDPT process. Moreover, the potential energy curves along the proton transfer coordinates are calculated to distinguish the sequence of the proton transfer and clarify the ESDPT reaction mechanism.

II. Experimental and theoretical methods

The 2-aminopyridine used in the present work was dissolved in polar and nonpolar solvents with a concentration of 5×10^{-4} mol L^{-1} at room temperature. The formic acid, acetic acid and propionic acid were selected as catalysts for the proton transfer reaction. Moreover, the hexane and acetonitrile were also used as solvents for comparison. All the solvents used in the experiment are high-performance liquid chromatography (HPLC) grade which could avoid the influence of water on the formation of the intermolecular hydrogen bonds. Steady-state absorption and fluorescence spectra were recorded on a HP-8453 spectrophotometer and a PTI-C-700 Felix and Time-Master system, respectively. The excitation wavelength was selected at 266 nm.

In the present work, all the electronic structure calculations were carried out using the Turbomole program suite.[53–59] The geometric optimizations of the monomer, the hydrogen-bonded 2AP/acetic acid complex were performed in the ground state using density functional theory (DFT) with Becke's three-parameter hybrid exchange function with the Lee–Yang–Parr gradient-corrected correlation (B3-LYP) functional. While in the electronic excited states, the geometric structures of the 2AP monomer, 2AP/acetic acid complex and corresponding proton transfer tautomer complex were optimized using the time-dependent density functional theory (TDDFT) with the same B3LYP hybrid functional. The TDDFT method has become a very useful tool to study the hydrogen bonding in the electronic excited states of the hydrogen-bonded systems theoretically.[8–15] There were no constraints to all the atoms, bonds and angles during the geometric optimization. Throughout the optimizations and

the energy calculations, the triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as the basis set.[56,57] Fine quadrature grids of size 4 were adopted.

III. Results and discussion

A Steady-state absorption and fluorescence spectra

Fig. 1 shows the steady-state absorption and fluorescence spectra of 2AP in various solvents. Although the steady-state spectral characters of 2AP in hexane and acetic acid have been measured in the previous works,[34,46–54] the spectral properties of 2AP in formic acid and propionic acid as well as in the hybrid solvent composed by acetic acid and acetonitrile have been given here for the first time. One can note that the absorption spectra of 2AP in all the solvents shown in Fig. 1a have two peaks at the spectral range of 200–250 nm and 280–300 nm, respectively. It is clear that the absorption peaks for both the S_1 and S_2 states are redshifted due to the formation of intermolecular hydrogen bonds between 2AP and various acids. Fig. 1b shows the fluorescence spectra of 2AP in various solvents. The fluorescence maximum of 2AP in hexane is at 322 nm. It is noted that there are two fluorescence peaks upon photoexcitation to the S_1 state of 2AP in hexane and acetic acid solvents. The fluorescence maximum is redshifted to 329 nm due to the formation of hydrogen bonds. Furthermore, a new fluorescence band appears near 420 nm. The fine structures of the band could be assigned as the vibrational structures. It has been demonstrated that the new fluorescence band is originated from the imino form of 2AP
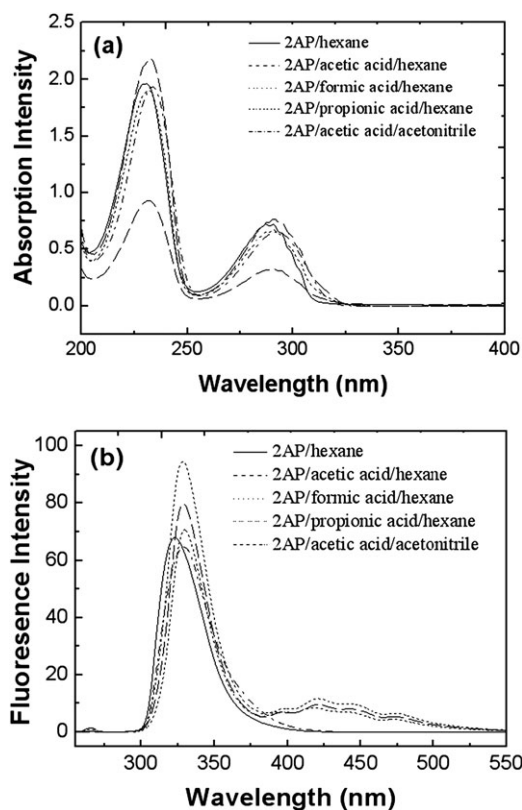
after ESDPT reaction. Therefore, it is distinct that the ESDPT takes place in the S_1 state of 2AP in acetic acid and hexane solvent. Moreover, there are also two fluorescence peaks in the fluorescence spectra of 2AP in formic acid and propionic acid solvents. Thus, we demonstrate for the first time that the ESDPT can also take place between 2AP and formic acid as well as propionic acid. So it is clear that the formation of the double intermolecular hydrogen bonds between 2AP and acids is a prerequisite for the ESDPT. It should be noted that the fluorescence band at around 420 nm disappeared in the fluorescence spectra of 2AP in acetic acid and polar acetonitrile solvent. This may be due to the fact that the respective polar solvation of 2AP and acids by the acetonitrile solvent disrupts the formation of intermolecular double hydrogen bonds between 2AP and acids. Hence, it can be confirmed that the formation of intermolecular double hydrogen bonds between 2AP and acids plays a very important role on the ESDPT process.

B Calculated electronic spectra

The calculated electronic excitation energies and corresponding oscillator strengths of the 2AP monomer and its hydrogen-bonded 2AP/acetic acid complex are presented in Table 1. From the comparison of the monomer and complex, one can note that the excitation energies for all the excited states of the complex are lower than the 2AP monomer correspondingly due to the intermolecular hydrogen bonding interaction between the 2AP and acetic acid. The experimental results indicate that the proton transfer reaction takes place in the S_1 state. The calculated S_1 absorption peak is located at 265 nm and 279 nm for the monomer and complex, respectively. The calculated results are in good agreement with the experimental results shown in Fig. 1. At the same time, the calculated fluorescence values are also listed in Table 1. One can distinctly find that the calculated fluorescence values of the hydrogen-bonded complex formed by 2AP and acetic acid and the proton-transferred complex are consistent with the fluorescence spectra of 2AP in acetic acid/hexane solvent. Thus, the ESDPT can be confirmed by the calculated fluorescence spectra.

C Geometric structures of 2AP/acetic acid system

We have optimized the geometric structures of the 2AP monomer and the 2AP/acetic acid complex and its tautomer in both the ground and electronic excited states with B3LYP

Fig. 1 Absorption and fluorescence spectra of the 2AP and 2AP/acid systems in hexane and acetonitrile solvents.

Table 1 Calculated electronic excited energies (in nm) and corresponding oscillator strengths of 2-aminopyridine (2AP) monomer as well as the 2-aminopyridine/acetic acid (2AP/acetic acid) complex

		2AP	2AP/acetic acid
S_1	Abs.	265(0.056)	279(0.063)
	Exp.	287	291
	Flu.	298(0.054)	327(0.047)/445(0.029)
	Exp.	322	329/420
S_2		243(0.003)	228(0.002)
S_3		218(0.136)	221(0.167)
S_4		216(0.035)	213(0.050)
S_5		207(0.030)	211(0.002)
S_6		186(0.000)	207(0.001)
S_7		180(0.045)	204(0.002)

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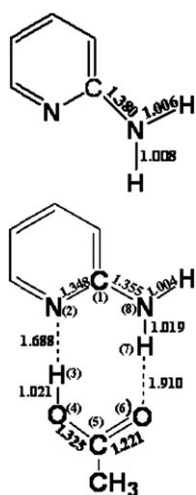*Phys. Chem. Chem. Phys.*, 2009, **11**, 4385–4390 | 4387

Fig. 2 Optimized geometric structures of the 2AP monomer and the hydrogen-bonded 2AP/acetic acid system in the ground state.

and TD-B3LYP methods, respectively. Fig. 2 shows the optimized ground-state geometric structures of 2AP and the hydrogen-bonded 2AP/acetic acid system. One can find that two strong intermolecular hydrogen bonds are formed in the 2AP/acetic acid complex. The calculated hydrogen bond length of O–H$\cdots$N and N–H$\cdots$O is 1.688 and 1.910 Å, respectively. At the same time, the length of C–N bond is correspondingly shortened, while that of the N–H bond is lengthened due to the formation of intermolecular hydrogen bonds.

The optimized excited-state geometric structures of isolated 2AP, the hydrogen-bonded 2AP/acetic acid complex and its tautomer are shown in Fig. 3. It can be noted that the N–H bond length is increased from 1.008 to 1.011 Å in the S_1 state of 2AP monomer. In the S_1 state of the hydrogen-bonded 2AP/acetic acid complex, the N–H bond continues to lengthen to 1.046 Å due to the formation of intermolecular hydrogen bond N–H$\cdots$O. Furthermore, the hydrogen bond length of
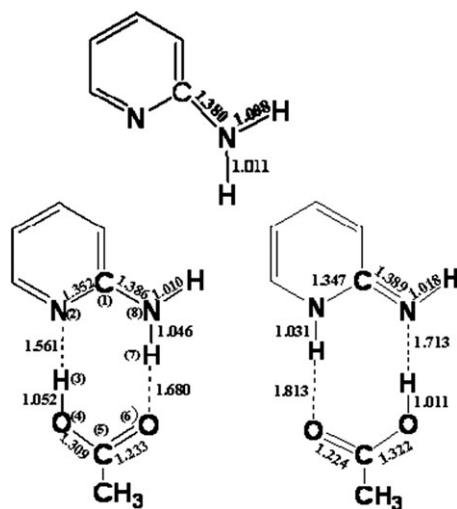

Fig. 3 Optimized geometric structures of the 2AP monomer, the hydrogen-bonded 2AP/acetic acid system, and its tautomer in the electronic excited state.

N–H$\cdots$O is significantly shortened from 1.910 to 1.680 Å. One can also note that the O–H bond in the hydrogen-bonded 2AP/acetic acid complex is lengthened in the S_1 state compared with that in the ground state. At the same time, the hydrogen bond length of O–H$\cdots$N is decreased markedly from 1.688 to 1.561 Å in the S_1 state. From the optimized geometric structures of the hydrogen-bonded 2AP/acetic acid complex in the S_1 state, one can clearly find that both the intermolecular hydrogen bonds O–H$\cdots$N and N–H$\cdots$O are significantly strengthened upon photoexcitation of 2AP to the S_1 state. In our previous studies, we have demonstrated that the hydrogen bond strengthening in the electronic excited state can facilitate the electron transfer (ET) and internal conversion (IC) processes.[8–15] Herein, the excited-state proton transfer process may be tightly associated with the intermolecular hydrogen bond strengthening in the electronic exited state, since the proton transfer process takes place through the intermolecular hydrogen bond. The excited-state double proton transfer should be initiated and facilitated by the intermolecular hydrogen bond strengthening in excited states. The optimized geometric structure of the tautomer in the S_1 state after proton transfers is also presented in Fig. 3. Two new intermolecular hydrogen bonds O$\cdots$H–N and N$\cdots$O–H are formed between the imino forms of 2AP and acetic acid. It is noted that the hydrogen bond lengths of both O$\cdots$H–N and N$\cdots$O–H in the S_1 state are much longer than those in the hydrogen-bonded amino 2AP/acetic acid complex. The excited-state double proton transfer is not easy to reverse in the S_1 state due to the weak intermolecular hydrogen bonds.

D Excited-state double proton transfer reaction mechanism

As mentioned above, the photoinduced excited-state double proton transfer reaction along two parallel hydrogen bonds is very significant in photochemistry. The fundamental question and the hot topic is the ESDPT reaction mechanism. In the 2AP/acetic acid system, two intermolecular hydrogen bonds between 2AP and acetic acid are formed. The ESDPT reaction takes place through the two intermolecular hydrogen bonds. However, the details of the proton transfer mechanism still need to be investigated. Whether the double proton transfer is concerted or stepwise has drawn a comprehensive controversy.

The potential energy curves are important for investigating the proton transfer reaction mechanism.[20] Fig. 4 shows the calculated potential energy curves along the proton transfer coordinates. The three types of potential energy curves are calculated and shown in Fig. 4a. Type 1 is in accordance with the stepwise 1 mechanism, in which the proton transfers along the hydrogen bond O–H$\cdots$N. The ground-state and excited-state potential energy curves are calculated and scanned by increasing the O–H bond length with a step of 0.1 Å. Type 2 accords with the stepwise 2 mechanism, in which the proton transfers along the hydrogen bond N–H$\cdots$O. The potential energy curves in both the ground state and electronic excited state are also calculated and scanned by increasing the N–H bond length with a step of 0.1 Å. Type 3 belongs to the concerted mechanism, in which the two protons begin to move simultaneously. In this case, it is proposed that the velocity of proton transfer in O–H$\cdots$N is approximately equal to that in

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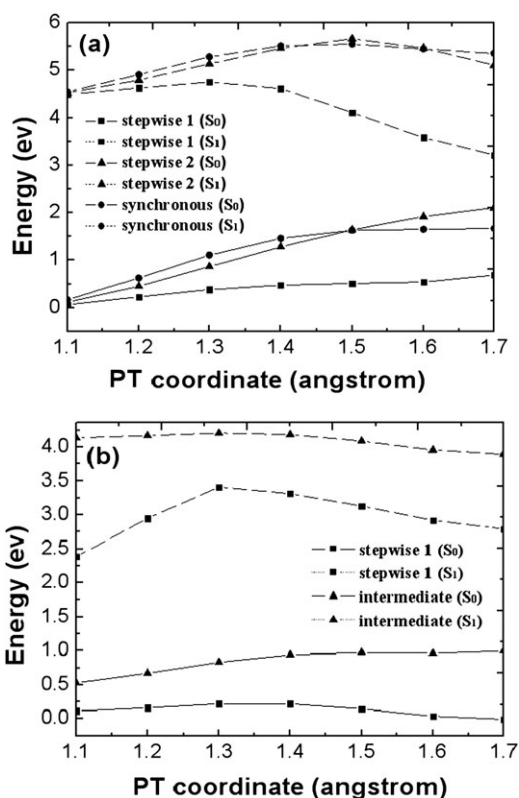This journal is © the Owner Societies 2009

Fig. 4 Calculated potential energy curves along the proton transfer coordinate with different mechanisms.

N–H···O. Hence, the lengths of both the O–H and N–H bonds are synchronously tuned with a step of 0.1 Å to calculate the potential energy curves. One can clearly see that the proton transfer reaction with stepwise 1 mechanism is nearly a barrierless process. Moreover, the other potential energy curves of the S_1 state have high barriers for the proton transfer reaction. Thus, it is clear that the first proton transfer along the hydrogen bond O–H···N is the most possible reaction channel.

To further confirm the stepwise mechanism and exclude the concerted mechanism, Fig. 4b shows additional potential energy curves along the second proton transfer coordinate. Type 1 denotes that the first proton has been transferred along the hydrogen bond O–H···N. Type 2 denotes that the first proton is located in the intermediate site of the hydrogen bond O–H···N. One can clearly note that the potential energy curve of both the ground state and S_1 state for the type 1 is always lower than that for the type 2. This indicates that the second proton begins to transfer when the first proton transfer is completed. Thus, the stepwise mechanism for the ESDPT process is confirmed again. At the same time, the concerted mechanism is excluded.

From our discussions above, it is evident that the intermolecular hydrogen bonding in the electronic excited state plays a very important role on the ESDPT process. Due to the excited-state strengthening of the intermolecular hydrogen bond O–H···N, the proton transfer in the excited state of 2AP/acetic acid system becomes a barrierless process. Hence, the proton transfer along the hydrogen bond O–H···N first
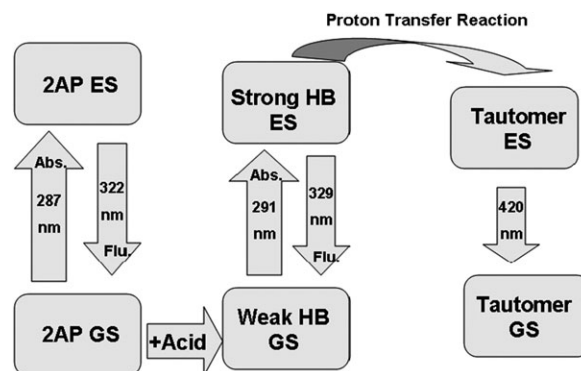

Fig. 5 The schematic view of the photochemistry of 2AP in different solvents.

takes place. Then, the second proton transfer along the hydrogen bond N–H···O is driven to occur after the first proton transfer. Thus, the ESDPT mechanism of the 2AP/acid systems is tightly associated with the nature of hydrogen bonding interactions in the electronic excited state.

Fig. 5 gives the schematic view of the photochemistry of 2AP in different solvents. When the 2AP is dissolved in nonpolar hexane solvent, only one fluorescence peak can be observed. All the absorption and fluorescence spectra correspond to the absorption and fluorescence spectra of the isolated 2AP molecule. After the acid solvents, such as formic acid, acetic acid, propionic acid etc., have been added into the 2AP/hexane solution, the intermolecular double hydrogen bonds between 2AP and acid solvents are formed. The proton transfer can not take place in the ground state. Upon photo-excitation, the intermolecular hydrogen bonds become significantly strengthened in the electronic excited state. The excited-state double proton transfer reaction is facilitated by the intermolecular hydrogen bond strengthening in the electronic excited state. Therefore, the amino and imino forms contribute to the two fluorescence peaks in the fluorescence spectra, respectively.

IV. Conclusion

In this work, the excited-state double proton transfer (ESDPT) reaction of the intermolecular hydrogen-bonded 2-aminopyridine/acid systems was investigated by both experimental and theoretical methods. In the experiment, the steady-state absorption and fluorescence spectra have been measured. The ESDPT reaction can be indicated by the new fluorescence peak at the red in the fluorescence spectra of 2AP in acetic acid. Moreover, we have demonstrated for the first time that the ESDPT reaction can also take place for 2AP in some other acids, such as formic acid, and propionic acid, etc. However, the ESDPT cannot occur for 2AP in acids with presence of polar acetonitrile solvent. This may be due to the fact that the intermolecular double hydrogen bonds between 2AP and acids are dramatically broken by the polar solvation. It is shown that the formation of the intermolecular double hydrogen bonds plays a fundamental role in the ESDPT reaction.

The ground-state and excited-state geometric structures are optimized using the density functional theory (DFT) and

time-dependent density functional theory (TDDFT) methods, respectively. Especially, the intermolecular double hydrogen bonds in the electronic excited state of the hydrogen-bonded 2AP/acetic acid system are investigated by the TDDFT method. It has been demonstrated that the intermolecular double hydrogen bonds are significantly strengthened in the electronic excited state. The ESDPT reaction is facilitated by the electronic excited-state hydrogen bond strengthening. In addition, the potential energy curves of both the ground state and electronic excited state along the proton transfer coordinate are also calculated using the TDDFT method. The stepwise mechanism of the ESDPT for 2AP in acids is reconfirmed in our work. At the same time, the sequence of the double proton transfers is theoretically clarified for the first time. We have demonstrated that the proton transfer along the intermolecular hydrogen bond O–H···N takes place first. Then the second proton transfer along the intermolecular hydrogen bond N–H···O begins to occur after the first proton transfer is completed.

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